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### (54) LITHIUM SECONDARY BATTERY

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery at low cost, high stability and high capacity by constituting an aqueous lithium secondary battery with the use of a specific positive electrode active material.

SOLUTION: The lithium secondary battery is composed of a cathode including an olivine-structure lithium iron complex compound with  $\text{LiFePO}_4$  as basic composition in a cathode active material, an anode with matter having lithium storage/desorption potential lower than the lithium iron complex compound as an anode active material, and aqueous electrolyte solution with lithium salt dissolved in water.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the drainage system lithium secondary battery which uses a water solution as the electrolytic solution in detail about the lithium secondary battery using the occlusion and the desorption phenomenon of a lithium.

[0002]

[Description of the Prior Art] Since the lithium secondary battery using the occlusion and the desorption phenomenon of a lithium is a high energy consistency, it has come to spread widely in the field of communication equipment and an information related equipment with the miniaturization of a cellular phone, a personal computer, etc. Moreover, also in the field of an automobile, development of an electric vehicle is hurried from the resource problem and the environmental problem, and the lithium secondary battery is examined also as a power source for these electric vehicles.

[0003] Generally the lithium secondary battery by which current utilization is carried out consists of a positive electrode which used the lithium transition-metals multiple oxide for positive active material, a negative electrode which used the carbon material etc. for the negative-electrode active material, and a nonaqueous electrolyte which dissolved lithium salt in the organic solvent, and has the 4V class high electrical potential difference for the mainstream.

[0004] However, since the above-mentioned lithium secondary battery uses the organic solvent of the low non-drainage system of the flash point for the electrolytic solution, ignition of the organic solvent and combustion pose a problem. Moreover, it is common to, equip devices, such as a PTC component and a relief valve, for example, for the purpose of there being a possibility that the electrolytic solution may decompose and inflammable gas may occur when it resulted in the overcharge condition, or when it is exposed to the bottom of hot environments, and securing safety. However, since an inflammable solvent is used, considerable difficulty hangs around for fully securing safety. Since the use under severe conditions, such as service temperature, is expected in addition to there being many amounts of the organic solvent used especially for the rechargeable battery as power sources for power, such as an automobile, being large-sized, higher safety is required.

[0005] Moreover, if moisture exists even when it is small in a cell, various problems, such as generating of the gas by the electrolysis-of-water reaction, consumption of the lithium by the reaction of water and a lithium, and corrosion of a cell component, will arise. For this reason, in manufacture of a lithium secondary battery, the thorough dry environment is needed, the special facility for removing moisture completely and a great effort are required, and this serves as a cause which pulls up the cost of a cell.

[0006] On the other hand, in the drainage system lithium secondary battery which used the water solution for the electrolytic solution, the above-mentioned problem is not generated fundamentally. Moreover, generally, since conductivity is good compared with a nonaqueous solution, as for a water solution, reaction resistance of a cell also decreases, and the output characteristics of a cell and a rate property improve. However, since the drainage system lithium secondary battery needs to carry out charge and discharge in the potential range in which an electrolysis-of-water reaction does not occur, it

holds the fault that it is difficult to secure a big discharge capacity as compared with a nonaqueous lithium secondary battery.

[0007] In addition to being stability in a water solution, from this, to use the active material which has a big capacity reversibly possible [ the occlusion and desorption of a lot of lithium ions ] that is, is desired with the drainage system lithium secondary battery in the potential range which neither oxygen nor hydrogen generates by the electrolysis of water.

[0008] As a drainage system lithium secondary battery currently examined from the former For example, as shown in the Patent Publication Heisei No. 508490 [ nine to ] official report, as shown in JP,12-77073,A, the cell using  $\text{LiMn}_2\text{O}_4$  and  $\text{VO}_2$  grade as a negative-electrode active material again, using  $\text{LiMn}_2\text{O}_4$  grade as positive active material The cell using the  $\text{LiV}_3\text{O}_8$  grade as a negative-electrode active material exists using  $\text{LiCoO}_2$ ,  $\text{Li}(\text{nickel}, \text{Co}) \text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  grade as positive active material.

[0009]

[Problem(s) to be Solved by the Invention] When this invention person performs various trials paying attention to an active material,  $\text{LiV}_3\text{O}_8$  and  $\text{VO}_2$  grade which are the  $\text{LiCoO}_2$ ,  $\text{Li}(\text{nickel}, \text{Co}) \text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  grade and negative-electrode active material which are the positive active material currently examined from the former Since it is difficult to take out sufficient capacity in the potential range in which an electrolysis-of-water reaction does not occur and there is a problem also in the stability in the inside of a water solution, When a drainage system lithium secondary battery was actually constituted using them, it turned out that the capacity and the cycle property of the lithium secondary battery are not what can be satisfied practical.

[0010] this invention person came to find out the positive active material which has a big capacity in cell voltage within the limits of a drainage system lithium secondary battery as a result of the further research on a drainage system lithium secondary battery, and a many thing experiment. By constituting a drainage system lithium secondary battery using the positive active material, this invention is low cost, and its safety is high and it makes it a technical problem to offer a lithium secondary battery with a large capacity.

[0011]

[Means for Solving the Problem] It is characterized by the lithium secondary battery of this invention coming to have the positive electrode which contains in positive active material the olivine structure lithium iron multiple oxide which sets a basic presentation to  $\text{LiFePO}_4$ , the negative electrode which uses the matter with lithium occlusion and desorption potential lower than the lithium iron multiple oxide as a negative-electrode active material, and the drainage system electrolytic solution which dissolved lithium salt in water.

[0012] That is, the lithium secondary battery of this invention is a rechargeable battery which used for positive active material reversibly the lithium iron multiple oxide in which the occlusion and desorption of a lot of lithium ions are possible in the potential range which uses cheap iron as the main configuration element, and the oxygen evolution by the electrolysis of water does not produce.

[0013] Although explained in detail later, when it produced the electrode which used the lithium iron multiple oxide of an example as the active material and the unipolar evaluation trial by the cyclic voltamogram was performed, the obtained current-potential curve (valve flow coefficient curve) showed that this lithium iron multiple oxide showed 2 so-called phase coexistence types in which only one has an oxidation reduction potential of lithium occlusion and desorption behavior. Namely, in the case of charge and discharge, in  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  from which a lattice constant etc. changes to continuation in connection with the occlusion and desorption of a lithium, and potential changes, it differs and, as for this lithium iron multiple oxide, the potential of abbreviation regularity is shown in the case of charge and discharge. And the potential of the charge and discharge was the 3.5V neighborhood (vs. $\text{Li}/\text{Li}^+$ ) which is potential within the limits which the oxygen evolution by the electrolysis of water does not produce. Moreover, since the standup of the peak of obtained valve flow coefficient curve was sudden and polarization was small, it also turned out that the reaction resistance in an oxidation reduction reaction is small.

[0014] From this, it can be said that the occlusion and desorption of a lot of lithium ions are reversibly possible for this lithium iron multiple oxide, and it is suitable as positive active material in a drainage system lithium secondary battery in the potential range which the oxygen evolution by the electrolysis of water does not produce.

[0015] Therefore, the lithium secondary battery of this invention which is the drainage system lithium secondary battery using this lithium iron multiple oxide as positive active material turns into a rechargeable battery excellent in large capacity and output characteristics, maintaining the advantage of the Takayasu all nature by being a drainage system lithium secondary battery, and low cost.

Furthermore, although it is having become clear in the next experiment, even if the lithium secondary battery of this invention repeats charge and discharge, its fall of capacity is small, and a cycle property, especially the cycle property under an elevated temperature serve as a good rechargeable battery.

[0016] Moreover, as for the lithium secondary battery of this invention, it is desirable to consider as the mode which contains in a negative-electrode active material the lithium vanadium multiple oxide which is the matter with lithium occlusion and desorption potential lower than the above-mentioned lithium iron multiple oxide. A lithium vanadium multiple oxide can constitute a 1V class rechargeable battery combining a lithium iron multiple oxide. Even if it has the peak of the highest reinforcement at  $2\theta = 13.9^\circ$  ( $\theta$  is an angle of diffraction) and the reinforcement of the peak compares with the reinforcement of which other peaks in the X diffraction pattern by CuK alpha rays especially, it is desirable to use the lithium vanadium multiple oxide which is 5 or more times.

[0017] Since the above-mentioned lithium vanadium multiple oxide suitable as a negative-electrode active material now has the small reinforcement of almost all the peaks that can be recognized from an X diffraction pattern, it has not been made clearly whether it is that in which the crystal structure has what kind of space group. Therefore, the above-mentioned lithium vanadium multiple oxide cannot carry out a clear definition as having a characteristic X diffraction pattern which was mentioned above. The X diffraction chart by the CuK alpha rays of the lithium vanadium multiple oxide used for the lithium secondary battery of an example explained later as an example of the X diffraction pattern is shown in drawing 1.

[0018] As shown in drawing 1, the peak of the highest reinforcement is in  $2\theta = 13.9^\circ$  ( $\theta$  is an angle of diffraction) with the X diffraction chart, and the reinforcement of other peaks except the peak is very low. The reinforcement of the strong highest peak is the reinforcement beyond the value which is the reinforcement of which other peaks and which was doubled five. It can \*\*\*\* having the crystal structure in which this lithium vanadium multiple oxide has the space group which carried out orientation to an one direction strongly from this X diffraction chart.

[0019] Although it can \*\*\*\* that it is a thing resulting from having the special crystal structure which was mentioned above, now, the exact reason has not performed clearly that this lithium vanadium multiple oxide shows a property good as a negative-electrode active material of a drainage system lithium secondary battery. However, according to the experiment explained in detail by the term of a next example, a capacity big to be sure is obtained at actuation cell voltage within the limits of a drainage system lithium secondary battery, and with this lithium vanadium multiple oxide, since it is arranged so that the configuration atom may carry out orientation to an one direction, this is considered that it originates in it and occlusion and desorption of a lithium are performed easily.

[0020] Moreover, since a curve also with a very flat charge-and-discharge curve is shown, it is thought that this lithium vanadium multiple oxide has what does not carry out phase transition to actuation cell voltage within the limits of a drainage system lithium secondary battery, i.e., the crystal structure without phase transition. It can recognize that this lithium vanadium multiple oxide can obtain a big capacity by actuation cell voltage within the limits, and serves as a suitable negative-electrode active material also by this. Moreover, it is good and stable also to the drainage system electrolytic solution, and also by the charge and discharge repeated further, there is no collapse of the crystal structure and a charge-and-discharge cycle property also serves as a negative-electrode active material which can maintain a big capacity.

[0021] Therefore, the lithium secondary battery of this invention of a mode using the above-mentioned

lithium vanadium multiple oxide as a negative-electrode active material turns into a lithium secondary battery with good large capacity and cycle property.

[0022]

[Embodiment of the Invention] Below, the operation gestalt of the lithium secondary battery of this invention is explained for every component.

[0023] <Positive active material> The olivine structure lithium iron multiple oxide which sets a basic presentation to  $\text{LiFePO}_4$  is contained in the positive active material of the lithium secondary battery of this invention. Here, it is the semantics of the typical presentation of a lithium iron multiple oxide with "a basic presentation is made into -", and not only the thing of the presentation expressed with the above-mentioned empirical formula but the presentation of what permuted a part of site of Fe in the crystal structure in part by one sort or two sorts or more of other elements, such as Co, nickel, Mn, and Mg, is included. Moreover, the cation atom of a lithium or iron which it is not necessarily limited to the thing of stoichiometric composition, for example, is produced unescapable on manufacture suffered a loss, or the thing of the non-stoichiometric composition to which the oxygen atom suffered a loss etc. is included.

[0024] Moreover, as for this lithium iron multiple oxide, the crystal structure turns into olivine structure of orthorhombic system, and the space group is expressed with  $\text{Pmnb}$ . That is, olivine structure is the structure where Lynn is located in the tetrahedron site and both a lithium and iron are located in an octahedron site on the basis of the hexagonal closest packing of oxygen.

[0025] Although especially this lithium iron multiple oxide does not restrict the particle diameter of the particle, when the occlusion and desorption of a lithium ion are made to react more smoothly and charge and discharge are carried out by the practical charge-and-discharge consistency, as for the mean particle diameter of the viewpoint of obtaining sufficient active material discharge capacity to the particle, it is desirable to be referred to as 1 micrometer or less. When production of an electrode takes into consideration especially the point that a rate property is good, easily, it is desirable to set mean particle diameter to 0.2 micrometers or more 0.8 micrometers or less.

[0026] In addition, a lithium iron multiple oxide is formed from the particle which exists in an abbreviation independent. Therefore, mean particle diameter is the average value of the particle size of the particle which exists in this abbreviation independent, and each particle size can be measured using the scanning electron microscope (SEM) photograph of for example, a lithium iron multiple oxide. That is, the SEM photograph of a lithium iron multiple oxide can be taken, the diameter of the longest and the diameter of the shortest of a lithium iron multiple oxide particle in the photograph can be measured, and the average of these two values can be adopted as a particle size of the one particle.

[0027] Especially this lithium iron multiple oxide does not limit the manufacture approach. For example, it can manufacture by the approach of consisting of a raw material mixing process of mixing a raw material and obtaining mixture, and a baking process which calcinates this mixture at predetermined temperature. Hereafter, each process is explained.

[0028] (1) The raw material mixing process in the manufacture approach of a raw material mixing process book lithium iron multiple oxide is a process which mixes a lithium compound, an iron compound, and the Lynn content ammonium salt, and obtains mixture.

[0029] As a lithium compound used as the source of a lithium,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and  $\text{LiNO}_3$  grade can be used. Since it says especially that reactivity is high, it is desirable to use  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

[0030] As an iron compound used as an iron source,  $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  and  $\text{FeCl}_2$  grade can be used as a compound whose iron valence is divalent. Since it says that corrosive [ of the gas which occurs especially at the time of baking ] is low, it is desirable to use  $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ .

[0031] As Lynn content ammonium salt used as the source of Lynn,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $2(\text{NH}_4)\text{HPO}_4$ , and  $\text{P}_2\text{O}_5$  grade can be used. Since it says especially that reactivity is high ( $\text{NH}_4$ ), it is desirable to use  $2\text{HPO}_4$ .

[0032] What is necessary is just to perform those mixing by the approach used for mixing of the usual fine particles that a powder-like thing should just be used for each above-mentioned raw material. What is necessary is just to specifically mix using a ball mill, a mixer, a mortar, etc. In addition, what is

necessary is just to let the mixed rate of each raw material be a rate according to the presentation of the lithium iron multiple oxide which it is going to manufacture.

[0033] Moreover, in order for a mean diameter to obtain the lithium iron multiple oxide used as 1 micrometer or less, it is desirable to control the mean diameter of the above-mentioned raw material, and it is desirable for a mean diameter to use a thing 1 micrometer or less especially in each raw material.

[0034] (2) A baking process baking process is a process which calcinates the mixture obtained at the raw material mixing process at 600-degree-C or more temperature of 700 degrees C or less. What is necessary is just to specifically perform it under an inert atmosphere or reducing atmosphere in the inside of an argon air current, or the nitrogen air-current middle class, in order for baking to prevent iron oxidizing to trivalent.

[0035] Burning temperature is made into 600 degrees C or more 700 degrees C or less. It is because a reaction does not fully advance that burning temperature is less than 600 degrees C, but subphases other than the thing of the prismatic crystal made into the purpose generate and the crystallinity of a lithium iron multiple oxide worsens. It is because the particle of a lithium iron multiple oxide will grow and sufficient property will no longer be acquired on the contrary, if it exceeds 700 degrees C. Moreover, when the homogeneity of a presentation is taken into consideration, after carrying out predetermined time temporary quenching at about 350 degrees C, you may calcinate in the above-mentioned temperature requirement. In addition, what is necessary is just to usually perform firing time for about 8 hours that what is necessary is just sufficient time amount to complete baking.

[0036] When using as positive active material of a lithium secondary battery, generally a powder-like thing is used for a lithium iron multiple oxide. Therefore, what was obtained by baking as mentioned above may grind, and manufacture of a cell may be presented with it.

[0037] <Negative-electrode active material> In the lithium secondary battery of this invention, the matter with lithium occlusion and desorption potential lower than the above-mentioned lithium iron multiple oxide is used for a negative-electrode active material. For example, it can do [ using a lithium vanadium multiple oxide, a lithium manganese multiple oxide, etc. or ]. Especially, since occlusion and the potential from which it is desorbed are suitable and a lithium is said that the stability in the inside of a water solution is good, it is desirable to use a lithium vanadium multiple oxide. A lithium vanadium multiple oxide can secure the electrical potential difference near 1V, when occlusion and the potential from which it is desorbed are 2.6-2.8V (vs.Li/Li+) and use a lithium ion combining the above-mentioned lithium iron multiple oxide reversibly. Since there is no collapse of the crystal structure and a big capacity can be maintained also by the charge and discharge repeated especially, even if it has the peak of the highest reinforcement at  $2\theta=13.9$  degree\*1 degree (theta is an angle of diffraction) and the reinforcement of the peak compares with the reinforcement of which other peaks, in the X diffraction pattern by CuK alpha rays, it is desirable to use the lithium vanadium multiple oxide which is 5 or more times.

[0038] Although especially a lithium vanadium multiple oxide does not limit the presentation, it is desirable that it is what is expressed with empirical formula  $\text{Li}_x\text{V}_3\text{O}_y$  ( $1.2 < x < 1.6$ ;  $7.5 \leq y \leq 8.25$ ). The thing of this presentation has the merit that the above-mentioned specific crystal structure can be acquired easily.

[0039] If the meaning of the presentation range is explained in detail, compared with the thing of the above-mentioned optimum range, in the case of  $x \leq 1.2$ , the stacking tendency to the one direction in the crystal structure becomes low, and in the case of  $x \geq 1.6$ , an impurity will generate, and it will bring about the capacity fall of a cell.

[0040] Speaking of the value of y, compared with the thing of the above-mentioned optimum range, the capacity fall resulting from the defect of the crystal structure becomes easy to arise in the case of  $y < 7.5$ , and, in the case of  $y > 8.25$ , possibility that transition of another crystal structure will arise increases.

[0041] Especially the lithium vanadium multiple oxide that has the above-mentioned presentation does not limit the manufacture approach. For example, the vanadium compound used as the lithium compound used as the source of a lithium and the source of vanadium can be mixed at a predetermined rate, and it can manufacture by calcinating mixture at predetermined temperature in a predetermined

ambient atmosphere.

[0042] As a lithium compound used as a raw material,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{LiNO}_3$ , and  $\text{Li}_2\text{SO}_4$  grade can be used.  $\text{V}_2\text{O}_5$  and  $\text{NH}_4\text{VO}_3$  grade can be used as a vanadium compound.